Crystal Indexing Method Using a Simulated Annealing Algorithm with Particular Applications in Nanocrystal Research

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ABSTRACT

The development of a crystal indexing computer program using interplanar angles and lattice spacings is very useful, particularly in nanocrystal research by transmission electron microscopy. However, the indexing involves a large number of possible variables, which prohibits the use of simple mathematical techniques. This article is concerned with an application of a combinatorial optimization technique using the simulated annealing algorithm for solving the crystal indexing problem where traditional descent optimization cannot be used. We show that the program can unambiguously identify the Miller indices using a set of interplanar angles even for crystals with low symmetry elements.

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Introduction

The science of nanoscale clusters, crystallites, and particles has attracted much attention in recent years.[1] Because the physical properties of the materials with diameters in the range of 1–50 nm would neither correspond to those of free atoms or molecules that make up the particles, nor to the bulk solids with identical composition, they have been shown to give interesting and unique electronic, optical, and magnetic properties. Although a variety of techniques have been developed to prepare nanosized materials, there are only a few techniques available for characterization. X-ray diffraction is by far the most popular method for the determination of crystal structures and lattice parameters; however, the diffraction lines of nanosized particles are so broad that they effectively ''disappear'' into the background radiation.[2]

At present, transmission electron microscopy (TEM) combined with electron diffraction (ED) in the modern electron microscope provides the most powerful technique for the characterization of nanosized materials. Because of the relatively short wavelengths associated with high energy electron beams, the image patterns can be used to measure the interplanar angles and the lattice spacings for identifying the Miller indices (MIs) of different crystal phases. This gives useful information about the phase orientation relationships, crystal twinning, crystal faulting, and the growth characteristics of small nano-sized materials.

However, nanocrystal indexing by TEM is not a simple task. Usually, indexing of selected phases is accomplished through a comparison of the measured angles and lattice spacings with a series of calculated data. Published tables of MIs with d-spacings and angles between crystallographic planes are available for high crystal symmetry systems (such as cubic and hexagonal crystals). Docherty et al.[3] were among the first to use a computer program, MORANG, to calculate the possible planes from the given interplanar angles with estimated measurement errors. Although this has greatly reduced the number of possible candidates for the matching process, the matching is still very tedious if more than two interplanar angles are involved.

In fact, the problem of identifying the set of MIs of a crystal from the measured interplanar angles can be formulated as an integer programming problem, with the cost function defined as the mismatch between a function of the measured angles and a function of the calculated angles. The global minimum of the cost function should correspond to the correct set of MIs. However, we also note that when the number of planes grows, the set of all possible MIs becomes factorially large, which is almost impossible to explore exhaustively. Also, traditional descent optimization techniques cannot be applied as the cost function and the solution spaces are not continuous functions. These types of problems are known as NP-complete combinatorial optimization problem,[4] which cannot be readily solved.

Recently, Tam and Compton[5] introduced a combinatorial optimization technique based on a genetic algorithm for searching the permissible MIs by best fitting experimental and calculated interplanar angles. They showed that the genetic algorithm can be successfully applied to index a low symmetry triclinic system. However, they restricted their permissible MI domain between -1 and 1. As the permissible MI space increases exponentially with the number of higher indices allowed, the inclusions of higher index planes become inevitably tedious in their chromosomal representations. In addition, extensive computing time was required using their investigation techniques.

In this article, we report a simple but effective combinatorial optimization algorithm, namely, the simulated annealing algorithm for the indexing crystal structures. This algorithm is based on the concept of the physical annealing process. A brief historical description of the technique is also given. We demonstrate that this algorithm can be successfully applied in the search of MIs for different crystal systems. The algorithm can easily take higher index planes into account and is therefore regarded as a more suitable and direct algorithm in solving the indexing problem. Indexing MIs of both hypothetical and experimental nanocrystals are also demonstrated in this article. We envisage that this optimization algorithm could be useful, particularly in nanocrystal research.

Interplanar Angles

It is well known that the interplanar angles are related to the Miller indices via some geometric formulas. For a different crystal system, a different

set of equations can be derived. These equations have been fully recorded in *International Tables for X-ray Crystallography*.[6] Lattice constants a, b, c, α, β, and γ and the reciprocal lattice constants, a^*, b^*, c^*, α^*, β^*, and γ^* are defined as usual.[6] The Miller indices of a plane are denoted by (h, k, l). The formulas for the triclinic, hexagonal, and monoclinic systems are summarized next.

TRICLINIC SYSTEM

The interplanar angle, ϕ, between two planes (hkl) and $(h'k'l')$ can be calculated as:

$$\begin{aligned}\cos\phi = [&hh'a^{*2} + kk'b^{*2} + ll'c^{*2} \\ &+ (kl^* + lk')b^*c^*\cos\alpha^* \\ &+ (lh' + hl')c^*a^*\cos\beta^* \\ &+ (hk' + kh')a^*b^*\cos\gamma^*]/\sqrt{Q_{hkl}Q_{h'k'l'}}\end{aligned} \tag{1}$$

where:

$$\begin{aligned}Q_{hkl} = {} & h^2a^{*2} + k^2b^{*2} + l^2c^{*2} + 2klb^*c^*\cos\alpha^* \\ & + 2lhc^*a^*\cos\beta^* + 2hka^*b^*\cos\gamma^*\end{aligned} \tag{2}$$

HEXAGONAL SYSTEM

The interplanar angle, ϕ, between two planes $(hk.l)$ and $(h'k.'l')$ is given as:

$$\cos\phi = \frac{[hh' + kk' + \frac{1}{2}(hk' + kh')]a^{*2} + ll'c^{*2}}{\sqrt{Q_{hk'l}Q_{h'k.'l'}}} \tag{3}$$

where:

$$Q_{hk.l} = (h^2 + k^2 + hk)a^{*2} + l^2c^{*2} \tag{4}$$

MONOCLINIC SYSTEM

The interplanar angle, ϕ, between two planes (hkl) and $(h'k'l')$ can be computed through the formula:

$$\cos\phi = \frac{hh'a^{*2} + kk'b^{*2} + ll'c^{*2} + (lh' + hl')c^*a^*\cos\beta^*}{\sqrt{Q_{hkl}Q_{h'k'l'}}} \tag{5}$$

where

$$Q_{hkl} = h^2a^{*2} + k^2b^{*2} + l^2c^{*2} + 2lhc^*a^*\cos\beta^* \tag{6}$$

Cost Function

In formulating an optimization problem, one of the key steps is to identify a suitable cost function so that, when it is minimized, its solution is the expected result. Here, it can be seen from the aforementioned relationships that the interplanar angles for a particular crystal system are a function of (hkl) and $(h'k'l')$ only, provided that the unit cell dimensions and the lattice parameters are given. Also, notice that for an angle between 0° and 180°, the cosine function is a single-valued function. Therefore, the cost function is defined as:

$$f(\mathbf{I}) = \sum_{i=1}^{nd} (\cos\phi_i - \cos\phi_i^{obs})^2 \tag{7}$$

where nd is the number of interplanar angles measured, $\mathbf{I}$ is the set of MIs, and the superscript *obs* denotes the measured angles.

Simulated Annealing Algorithm

The term ''annealing'' refers to the process in which a solid material is first melted and then allowed to cool by slowly reducing the temperature. Particles within the system attain a ground state arrangement which can be considered as a global minimum of its potential energy function at each temperature, T. However, if the system is cooled quickly, it will not reach the ground state but rather ends up in a polycrystalline or amorphous state having somewhat higher energy. The solidified material may be reheated and cooled slowly with the hope that it will then migrate to a lower energy state. In nature, the energy states of a system follow the so-called Boltzmann probability distribution which expresses the idea that a system in thermal equilibrium at temperature T has its energy probabilistically distributed among all different energy states. Metropolis et al.[7] were the first to incorporate this principle into numerical calculations by employing the Monte Carlo method to simulate the evolution to thermal equilibrium of a solid for a fixed temperature, T. This idea has been extended further to form the basis of the simulated annealing algorithm, which was first

proposed by Kirkpatrick et al.,[8] and independently by Cerny.[9] Specifically, the simulated annealing algorithm is a stochastic computational technique that can be applied for finding global or near global minimum solutions to large optimization problems.

Here, the cost function, $f(\mathbf{I})$, defined by eq. (7), can be regarded analogously as the energy state of a system that follows the Boltzmann probability distribution. A biased random walk in the MI space is implemented to search for the minimum cost function. During the search, some of the MIs are randomly perturbed and acceptance depends on the Boltzmann probabilistic distribution given below. The perturbation process is repeated until the system reaches its allowed final temperature. If $f(\mathbf{I})$ attains a reasonably small value, the assignment may represent the global solution. The structure of the algorithm is given as follows:

Initialization
  Generate an initial set of Miller indices, **I**.
  Select an initial , ε, N_c, and N. Input N_p and other parameters.
Cooling
For $i = 1, \ldots, N_c$
  Iterate = 0.
  Searching
  1) Index = random{0, 1}, p = random{1, . . . , N_p}, $\mathbf{I}' = \mathbf{I}$.
  2) If Index = 1,
     H'_p = random{−4, 4}, k'_p = random{−4, 4}, l'_p = random{−4, 4}.
  3 If Index = 0,
     randomly accept either h'_p, k'_p or l'_p = random{−4, 4}.
  4) If (000), goto 2.
  5) Calculate $\delta = f(\mathbf{I}') - f(\mathbf{I})$.
     If $\delta < 0$, then $\mathbf{I} = \mathbf{I}'$;
     else if random[0, 1] $< T \exp(-\delta/T)$, then $\mathbf{I} = \mathbf{I}'$.
  6) Iterate = Iterate + 1; goto 1 until Iterate > N.
$T = \varepsilon T$.

In the algorithm, the variables T, ε, and N_c represent the current temperature, cooling speed, and number of cooling steps, respectively. N_p indicates the number of planes to be indexed and N is the number of random perturbations in **I** per each cooling step. All uniformly distributed random numbers are generated using an established routine.[10] The expression $\{a, b\}$ is used to denote an integer number ranging from a to b, whereas the expression with the square bracket indicates a real, continuous value.

For each cooling step, N searching steps are executed. In each searching step, the MIs of a plane are randomly selected for perturbation. The modification, which is implemented in a random fashion, can be either all indices (h, k, and l) or just one being replaced by random number(s). If the perturbed solution $\mathbf{I}'$ contains any illegal index (000), the searching step is reiterated. Subsequently, the cost function of $\mathbf{I}'$ is evaluated. If the new function value is less than the previous one, the new move is accepted ($\mathbf{I} = \mathbf{I}'$). Otherwise, the acceptance of the perturbed solution is dependent on a Boltzmann probabilistic distribution chosen by numerical experiences as:

$$P = T \exp\left(\frac{f(\mathbf{I}) - f(\mathbf{I}')}{T}\right) \tag{8}$$

If a random number generated is less than P, the new move is accepted. Otherwise, control will pass to the next search step. The temperature of the system is updated after N search steps. The cooling process is repeated until the temperature of the system reaches the final value. Then, the solution, **I**, is reported as the assigned MIs.

The program begins with a relatively high temperature T to avoid premature entrapment at local minima. As T starts to decrease, the chance of rejecting an upward move in the cost function will increase. When the temperature become very low, the efforts to reduce the cost function further will

become very discouraging, which signals to terminate the annealing procedure. As the number of planes increases, a larger number of searching steps, N, may be helpful to converge to the global solution. It should be pointed out that there is no rigorous rule governing the selection of the initial temperature, the cooling speed, and the number of searching steps, N. These annealing parameters themselves have to be optimized by experience with regard to convergence speed.

Results

In all the test cases reported in what follows, the initial temperature, T, and the cooling speed were chosen by numerical experience as 0.5 and 0.9, respectively. The maximum cooling step, N_c, was taken to be 30. If the maximum cooling step exceeded without reaching the global minimum, the procedure was restarted with a higher number of iterations N per each cooling step. The computer time was estimated using a Sun Sparc workstation.

HYPOTHETICAL HEXAGONAL AND TRICLINIC CRYSTALS

The algorithm was tested using some hypothetical crystals of hexagonal and triclinic systems. In these cases, we deliberately chose a wide range of parameters and interplanar angles to verify the algorithm. The lattice parameters used to generate the corresponding interplanar angles are given in Table I. For each crystal system, the interplanar angles (up to two decimal places) were deliberately chosen as shown in Table II. We found that the algorithm could produce the global minima very quickly if the exact angles were used. For practical purposes, we believe the angles will be measured with a certain degree of error. Therefore, random noise of magnitude up to $\pm 0.5°$ is added to the interplanar angles to imitate the error in measurements. We found that the computer-program-generated MIs agreed perfectly with the theoretical calculations showing the robustness of the method. Typical convergence histories of the algorithms were obtained as shown in Figures 1 and 2. Both figures show that a large fluctuation in cost function is observed when T was high. As T decreased, more steps were rejected and thus the fluctuation decreased significantly. Also, it can be seen that the cost function decreased gradually as the cooling step increased. These are typical behaviors of a simulated annealing algorithm. Here, in both cases, N was chosen to be 40,000. The cpu time for the hexagonal crystal was about 4 minutes, whereas for the triclinic crystal it took about 13 minutes to finish the plane indexing.

TABLE I.
Crystallographic Data Used for the Hypothetical Crystals.

System	Triclinic	Hexagonal
a (Å)	14.16	14.10
b (Å)	21.32	13.07
c (Å)	13.07	21.90
α (°)	99.92	90.000
β (°)	92.68	90.000
γ (°)	106.15	120.000

TABLE II.
Interplanar Angles of the Hypothetical Crystals.

Planes[a]	Hexagonal (ϕ^{obs})	Triclinic (ϕ^{obs})
1 ∧ 2	24.46	86.55
1 ∧ 3	34.36	58.85
1 ∧ 4	109.50	55.69
1 ∧ 5	74.09	88.55
1 ∧ 6	128.53	136.14
2 ∧ 3	40.07	48.87
2 ∧ 4	128.77	73.86
2 ∧ 5	98.29	3.95
2 ∧ 6	120.89	50.72
3 ∧ 4	90.12	25.32
3 ∧ 5	83.52	47.61
3 ∧ 6	94.32	82.17
4 ∧ 5	55.16	72.24
4 ∧ 6	58.86	97.31
5 ∧ 6	113.96	48.19
Expected indices[b]	1: (010); 2: (23$\bar{1}$); 3: (134); 4: ($\bar{1}$02); 5: ($\bar{4}$31); 6: (1$\bar{2}$3)	1: (010); 2: ($\bar{3}$12); 3: ($\bar{1}$34);, 4: (123); 5: ($\bar{4}$13); 6: ($\bar{1}$2$\bar{1}$)
Expected f(I) values	1.6330×10^{-4}	2.1441×10^{-4}

[a] The "∧" symbols denote the interception between two crystal planes.
[b] The numbers are arbitrarily assigned to the expected indices for identification purposes.

PRACTICAL HEXAGONAL, TRICLINIC, AND MONOCLINIC SYSTEMS

The algorithm was tested using some realistic crystals of hexagonal, triclinic, and monoclinic systems as given in the study by Bishop.[11] The lattice parameters are given in Table III. For each crystal

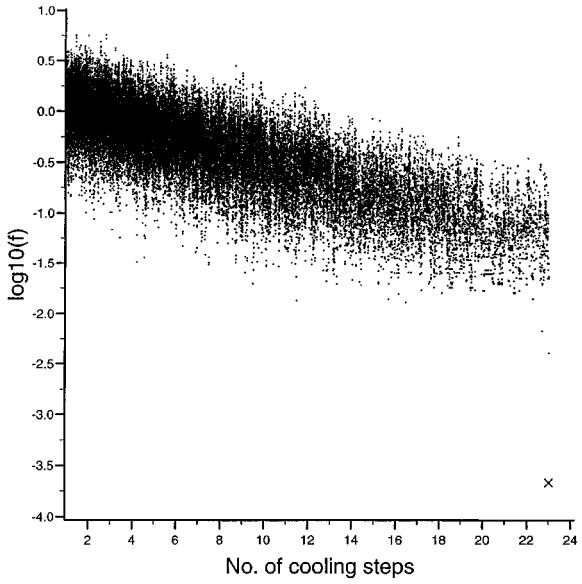

FIGURE 1. The convergence history of the algorithm for the hypothetical triclinic crystal.

system, the interplanar angles (up to two decimal places) are shown in Table IV; also, the shapes and the MIs for the chosen hexagonal, triclinicclinic crystals are shown in Figures 3, 4, and 5, respectively. In all cases, N was chosen to be 200,000. The cpu time for the hexagonal crystal was about 36 minutes and the procedure converged in the 19th cooling step. For the triclinic crystal, the cpu time taken was about 39 minutes, which con-

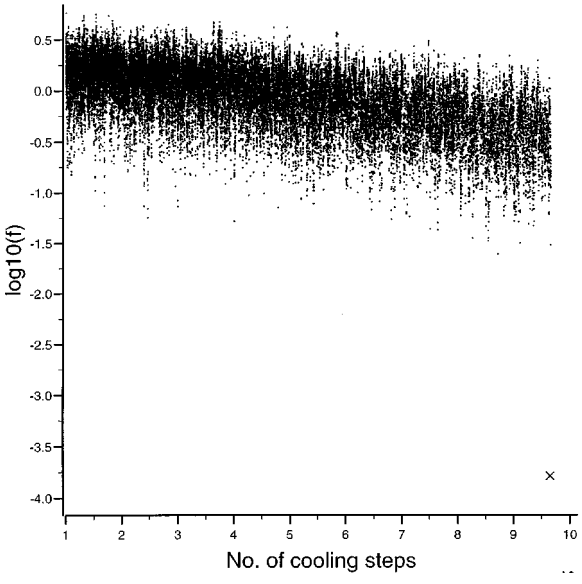

FIGURE 2. The convergence history of the algorithm for the hypothetical hexagonal crystal.

TABLE III.
Crystallographic Data Used for the Crystals.

System	Triclinic (Rhodonite[a])	Hexagonal (Vanadinite[b])	Monoclinic (Scolecite[c])
Space group	$P\bar{1}$	$P6\,(3)\,/\,m$	$P2$
a (Å)	7.699	10.331	9.850
b (Å)	12.220	10.331	18.980
c (Å)	6.702	7.343	6.520
α (°)	93.975	90.000	90.000
β (°)	93.067	90.000	110.100
γ (°)	68.200	120.000	90.000

[a] $Mn_2Si_2O_6$, PDF 13-138.
[b] $Pb_5(VO_4)_3Cl$, PDF 13-585.
[c] $CaAl_2Si_3O_{10} \cdot 3H_2O$, PDF 26-1048.

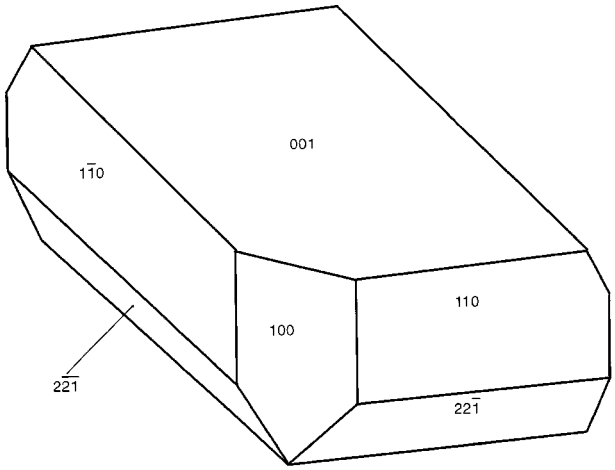

FIGURE 3. The triclinic crystal (Rhodonite).

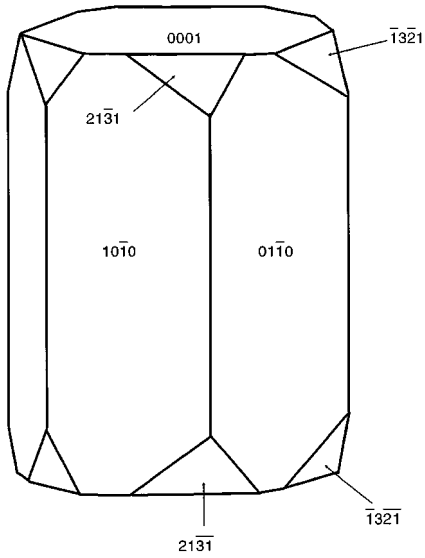

FIGURE 4. The hexagonal crystal (Vanadinite).

TABLE IV.
Interplanar Angles of the Crystals.

Planes[a]	Triclinic (Rhodonite) ϕ^{obs}	Hexagonal (Vanadinite) ϕ^{obs}	Monclinic (Scolecite) ϕ^{obs}
1 ∧ 2	90.15	65.27	45.06
1 ∧ 3	88.28	65.27	43.04
1 ∧ 4	86.22	90.00	45.06
1 ∧ 5	111.52	90.00	28.93
1 ∧ 6	116.05	114.73	28.93
1 ∧ 7	—	114.73	90.00
1 ∧ 8	—	—	90.76
1 ∧ 9	—	—	90.76
2 ∧ 3	25.43	54.02	14.89
2 ∧ 4	62.81	30.88	29.78
2 ∧ 5	21.37	46.64	42.06
2 ∧ 6	65.62	49.45	60.40
2 ∧ 7	—	76.26	104.89
2 ∧ 8	—	—	127.42
2 ∧ 9	—	—	134.90
3 ∧ 4	37.38	80.12	14.89
3 ∧ 5	33.98	30.88	50.23
3 ∧ 6	45.53	76.26	50.23
3 ∧ 7	—	49.45	90.00
3 ∧ 8	—	—	132.81
3 ∧ 9	—	—	132.81
4 ∧ 5	66.35	60.00	60.40
4 ∧ 6	29.83	30.88	42.06
4 ∧ 7	—	80.12	75.11
4 ∧ 8	—	—	134.90
4 ∧ 9	—	—	127.41
5 ∧ 6	57.04	46.64	57.85
5 ∧ 7	—	30.88	118.93
5 ∧ 8	—	—	85.36
5 ∧ 9	—	—	95.97
6 ∧ 7	—	54.02	61.07
6 ∧ 8	—	—	95.97
6 ∧ 9	—	—	85.36
7 ∧ 8	—	—	101.02
7 ∧ 9	—	—	78.98
8 ∧ 9	—	—	22.04
Expected indices[b]	1: (001); 2: $(1\bar{1}0)$; 3: (100); 4: (110); 5: $(2\bar{2}\bar{1})$; 6: $(22\bar{1})$	1: (0001) 2: $(21\bar{3}1)$; 3: $(\bar{1}3\bar{2}1)$ 4: $(10\bar{1}0)$; 5: $(01\bar{1}0)$; 6: $(21\bar{3}\bar{1})$; 7: $(\bar{1}3\bar{2}\bar{1})$	1: (100); 2: $(1\bar{1}1)$; 3: (101); 4: (111); 5: $(1\bar{1}0)$; 6: (110); 7: (010); 8: $(1\bar{1}\bar{2})$; 9: $(11\bar{2})$
Expected $f(\mathbf{I})$ values	1.8608×10^{-4}	2.7696×10^{-4}	4.1902×10^{-4}

[a] The "∧" symbols denote the interception between two crystal planes.
[b] The numbers are assigned to the expected indices arbitrarily for identification purposes.

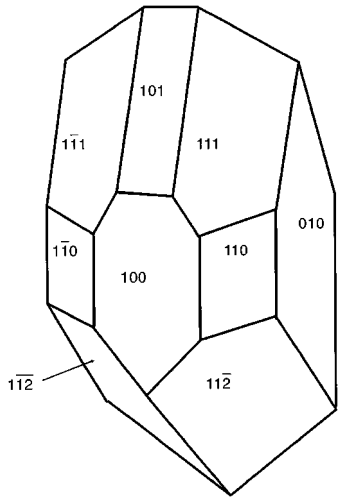

FIGURE 5. The monoclinic crystal (Scolecite).

verged in the 18th cooling step. Finally, for the monoclinic crystal, the cpu time used was about 83 minutes and it converged in the 14th step. We note that, for these three cases, the highest index never reached 4 or -4; therefore, a lot of unnecessary cpu time was used in searching the high indexing planes. Thus, we modified the searched indices between -2 and 2 in the monoclinic system and found that the cpu time reduced to 17 minutes with the convergency in the third step. For the hexagonal and triclinic crystals, the searched indexes fell to between -3 and 3, and the cpu times were found to be 14 and 6 minutes with the convergency in the 18th and 10th steps, respectively. Note that, in these two cases, N was chosen to be 80,000 for the hexagonal crystal and 50,000 for the triclinic crystal.

NANOCRYSTAL

In the final example, we demonstrate the use of the simulated annealing algorithm for the indexing of a nanocrystal. Figure 6 shows a high resolution TEM micrograph of a nanosized lathanium-containing crystal inside a carbon nanotube. This was made by filling the opened nanotubes with lathanium nitrate solution and then heated to 500°C under a flowing stream of oxygen. From our previous study we found that by filling the opened nanotubes with metal nitrate solution, followed by subsequent heat treatment in air, nanocrystals of metal oxides can be made. Generally, the thermodynamically most stable phase of metal oxide is made under these conditions.[12] The nanocavity of the tubes provided templates for the deposition of metal nitrate which was thought to decompose to the corresponding lanthanium oxide at the elevated temperature. The crystal was too small to cause detectable X-ray diffraction. Interplanar distances of 3.60 Å, 2.75 Å, and 2.75 Å with the interplanar angles of $1 \wedge 2 = 65°$, $1 \wedge 3 = 50°$, and $2 \wedge 3 = 65°$ associated with the crystal were measured from the projected images in the TEM micrograph. We employed the stable monoclinic lanthanum oxide phase in the program where the lattice parameters were obtained from the standard PDF files (the unit cell parameters of $a =$ 14.60 Å, $b = 3.717$ Å, $c = 9.278$ Å, $\alpha = 90°$, $\beta =$ 99.85°, $\gamma = 90°$). The interplanar distances and the angles obtained from the calculation agreed very well with the experimental results as the measurements were fed into the program. Thus, Miller's index plane can therefore be fixed from the corresponding lattice distances/angles. On the other hand, the results did not agree with the experimental measurements when the parameters of the cubic or other phases were used. The first Miller index plane was fixed to be (202) and was verified by the corresponding lattice distance. Upon inputting the measured angles into the program, the Miller indices of the second plane of $(\bar{1}12)$ and the third plane of $(\bar{3}03)$ were found. These matched with the d-spacings mentioned previously by only taking 2.5 seconds of cpu time and the algorithm was converged in the first cooling step. We have found that the same indexing planes were generated, even when feeding the error deviations of interplanar angle and spacing of $\pm 0.5°$ and ± 0.05 Å, respectively, into the program.

Conclusions

A crystal indexing program using the stimulated annealing algorithm has been developed. Using experimentally measured interplanar angles, the program is able to index crystal planes and spends reasonably little computer time without involving the tedious manual matching work. The program is also particularly useful for application in the area of nanocrystal research using the TEM technique in which the interplanar distances and angles can be obtained by electron crystallography.

The programs used herein and example datafiles can be obtained from K.F.C.Y. upon request.

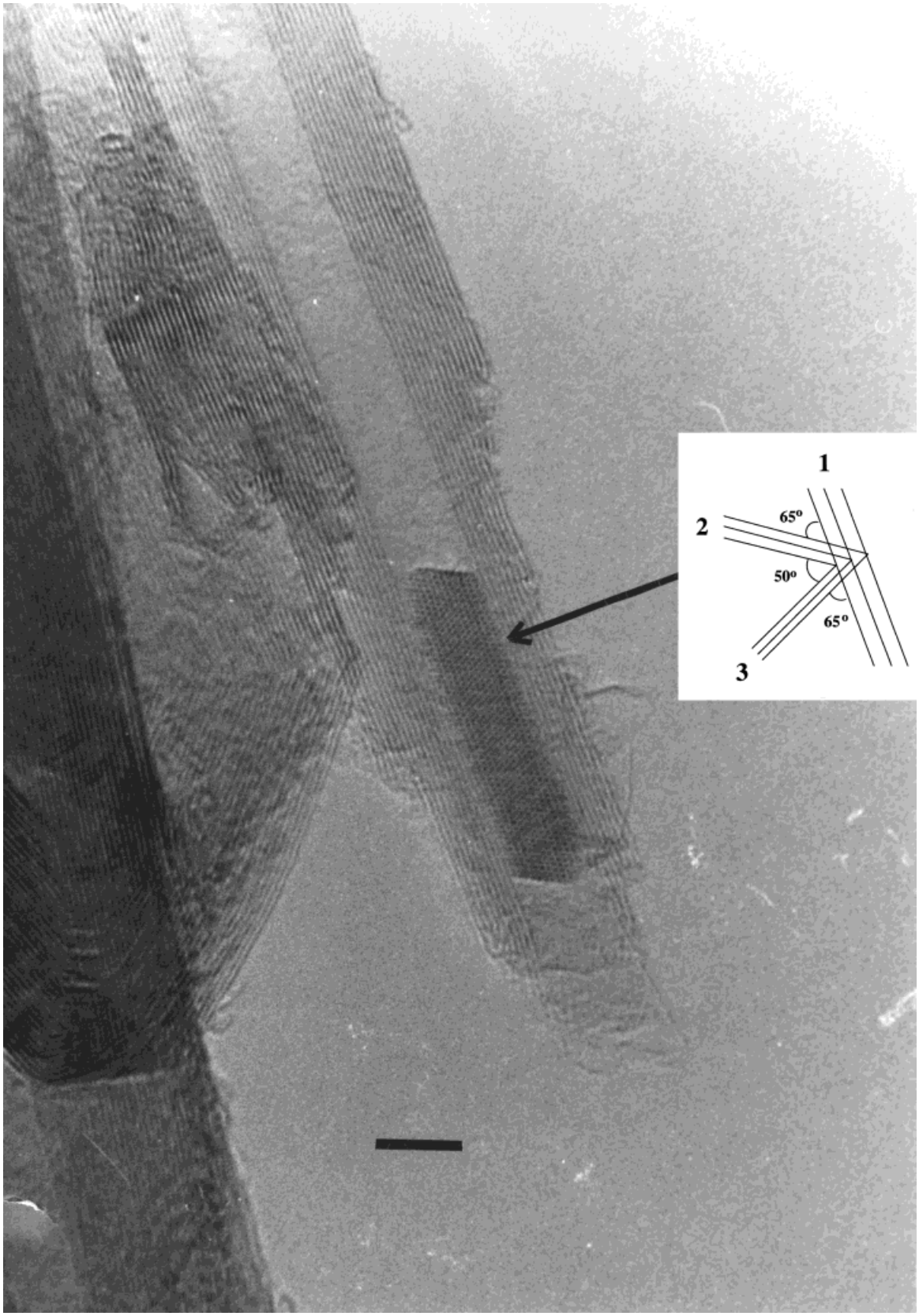

FIGURE 6. A high-resolution TEM micrograph of a lathanium oxide nanocrystal inside a carbon nanotube (the scale bar represents 50 Å).

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